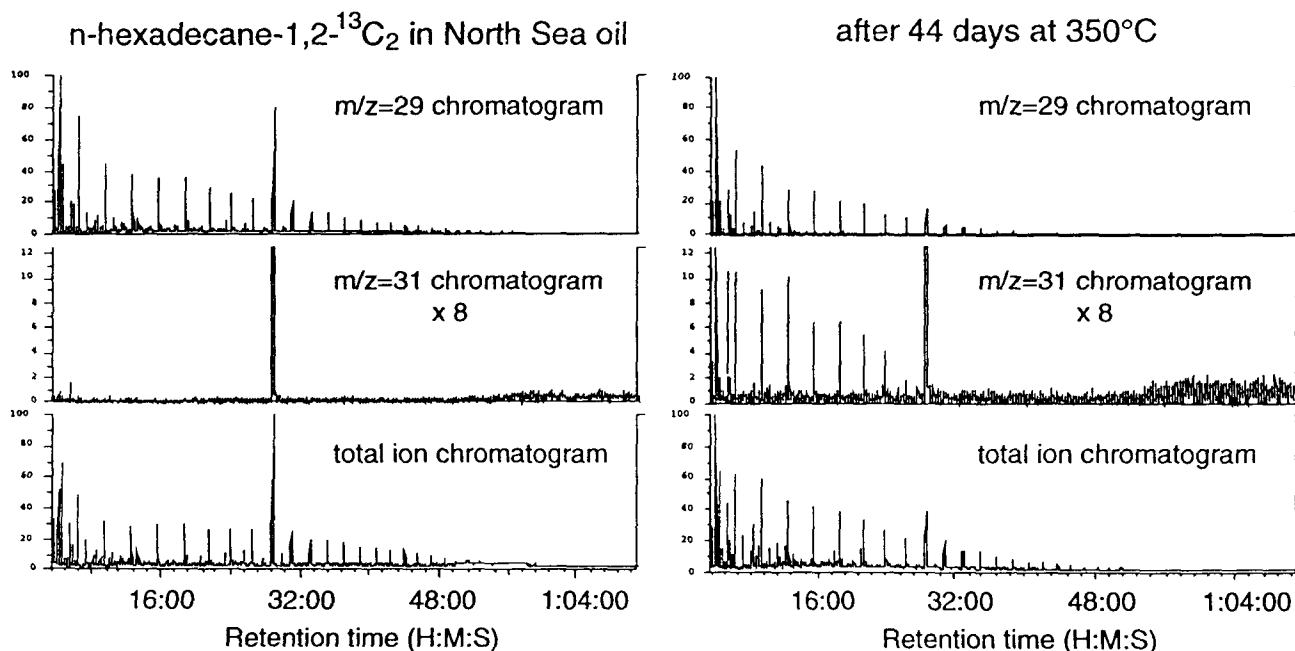


Unraveling the Kinetics of Petroleum Destruction by Using 1,2- $^{13}\text{C}_2$ Isotopically Labeled Dopants
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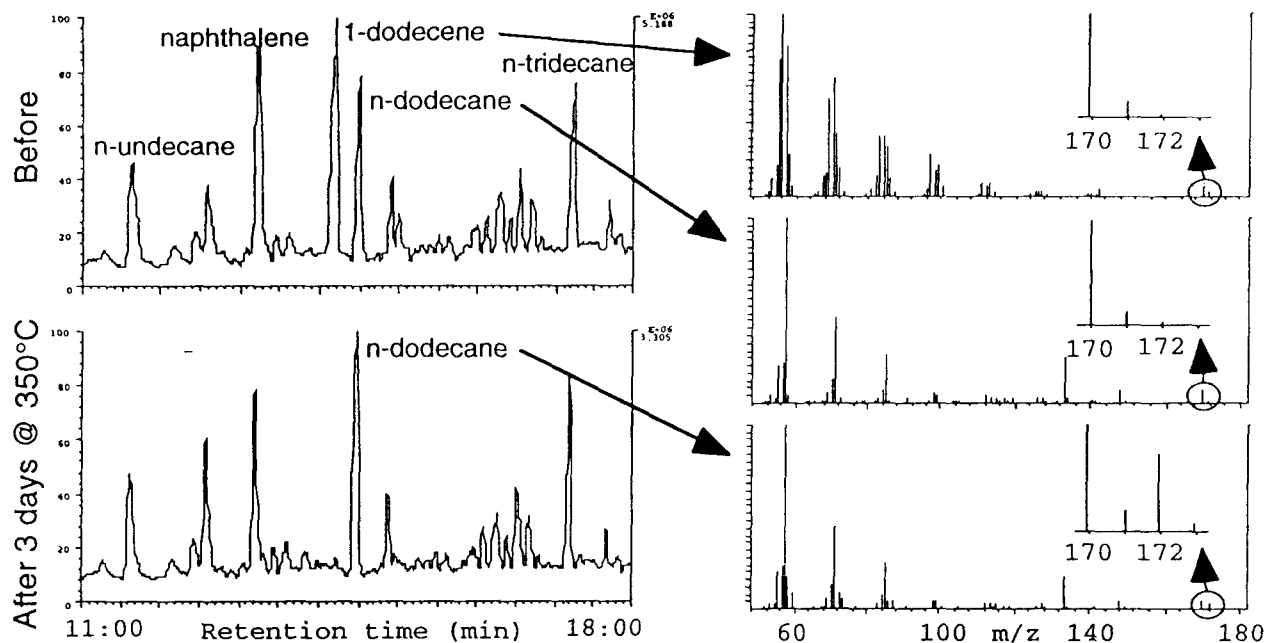
The stability of crude oil in the subsurface is of continuing interest as the search for new supplies pushes new frontiers.¹⁻⁴ Beyond mere stability, some investigators are developing kinetic models that would predict oil composition as well as occurrence.⁵⁻⁸ Two problems arise when deriving these compositional models: (1) it is difficult to unravel the reactions that simultaneously create and destroy a particular component in a complex mixture, and (2) the reactions of a given component by itself are not necessarily the same as in a complex matrix. A new isotopic method involving a double- ^{13}C label detected by gas chromatography-mass spectrometry (GC-MS) is presented here for unraveling these reactions.

The use of isotopic labels in kinetic studies is common (e.g., Hoering⁹) but investigations of skeletal reactions usually use a single labeled atom. A double- ^{13}C isotopic label is much easier to follow in an oil matrix by conventional GC-MS. The natural abundance of ^{13}C is 0.011, so the normal probability of finding two ^{13}C atoms in a small mass spectrometric fragment is very small: 0.00012 for a ethyl radical ($m/z = 31$) and 0.00036 for a propyl radical ($m/z = 45$). This low natural abundance makes it possible to follow both the disappearance and the appearance of doubly labeled species at very low dopant levels. A 1 wt % dopant of n-hexadecane-1,2- $^{13}\text{C}_2$ is easily detected in a $m/z = 31$ chromatogram with a signal-to-noise ratio of several hundred. Even though the added ^{13}C is only 10% of the total ^{13}C in the oil, it represents 99% of all mass 31 ethyl groups in the oil.

Procedure: One percent of a carbon-13 labeled spike (n-hexadecane-1,2- $^{13}\text{C}_2$ or 1-dodecene-1,2- $^{13}\text{C}_2$ both from Isotec, Inc., Miamisburg, OH) was added to three dissimilar oils (a North Sea oil: 38.4° API gravity, 0.2 wt % S, 46% saturates; a high paraffin oil: 42.5° API gravity, 0.03 wt % S, 71% saturates; a high sulfur oil: 25.4° API gravity, 3.3 wt % S, 28% saturates) and n-hexadecane. A two microliter aliquot was added, along with space filling glass beads, to capillaries (internal volume ~20 μL). The capillaries were sealed with a torch, and pyrolyzed in GC ovens at temperatures from 280°C to 360°C for periods of hours to over a year. The capillaries were then broken open, rinsed with methylene chloride, and transferred to a clean vial for analysis by GC-MS.



The $m/z=31$ mass chromatogram in the unreacted hexadecane/oil mixture is void of interferences. After pyrolysis of the mixture, $m/z=31$ clearly indicates that the labeled hexadecane was cracked into lighter n-alkanes.



The double label also allows us to track reactions by following the appearance or disappearance of $(M+2)^+$. Experiments with dodecene in oil show that one of the dominant reactions of dodecene is simple hydrogenation. Other experiments, spiking dodecene into hexadecane, shows the creation of dodecene-hexadecane adducts. Without the hydrogen donors found in oils, dodecene reacts with the matrix to form branched alkanes.

Identifying and following the creation and destruction reactions in complex matrices is nearly impossible without using isotopically labeled dopants. Reactions of a compound with a single ^{13}C label can be followed using GC-combustion-isotope-ratio MS; however many operators of these instruments don't want to "contaminate" their stable isotope instruments with "large" levels of carbon-13. The method presented here, using a double ^{13}C label, allows us to use traditional (i.e. relatively inexpensive) GC-MS to follow several reactions. The cost of the ^{13}C labeled compounds is quite small (and very little is needed) compared to the cost of a stable isotope mass spectrometer.

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